

ART 100/101
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Claims

1. A method of solubilizing carbon nanotubes, comprising the steps:
 - a) providing, in any order:
carbon nanotubes, and
urea as a precursor of isocyanic acid and/or cyanate ion, said isocyanic acid and/or cyanate ion being capable of undergoing a polymerization reaction;
 - b) mixing together the nanotubes with urea;
 - c) initiating a polymerization reaction of the isocyanic acid and/or cyanate ion to yield modified carbon nanotubes, wherein the carbon nanotubes have functional groups on their surface and/or ends, and wherein said polymerization reaction occurs at said functional groups.
2. The method according to claim 1, wherein the functional groups are oxygenated functional groups selected from the group comprising C-O species (alcohol, phenol, ether, epoxide), C=O species (aldehyde, ketone, quinone), and O-C=O species (carboxylic acid, ester, anhydride, lactone, pyrone).
3. The method according to any of the foregoing claims, wherein the carbon nanotubes are single-walled or multi-walled nanotubes.
4. The method according to any of the foregoing claims, wherein approximately 1 per 200 to 1 per 10 carbon atoms of the carbon nanotubes are in an oxidized state.
5. The method according to any of the foregoing claims, wherein approximately 1 per 150 to 1 per 20 carbon atoms of the carbon nanotubes are in an oxidized state.
6. The method according to claim 5, wherein approximately 1 per 100 carbon atoms of the carbon nanotubes are in an oxidized state.
7. The method according to any of the foregoing claims, comprising the additional step(s):
 - ba) heating the mixture, or, alternatively,
 - bb) acidifying the mixture or,

both steps ba) and bb).

8. The method according to claim 7, wherein the heating and/or acidifying is such, that the precursor of the at least one type of monomer molecules is induced to form said monomer molecules.
9. The method according to any of the foregoing claims, wherein the at least one type of monomer molecules or the precursor of the at least one type of monomer molecules is provided in a solvent.
10. The method according to any of the foregoing claims, wherein the carbon nanotubes are provided in a solvent.
11. The method according to claims 9 – 10, wherein the solvent of claim 9 is the same as the solvent of claim 10, or wherein the solvents are different.
12. The method according to any of claims 9 – 11, wherein the solvent(s) can be heated to a temperature close to or above the melting point of the monomer or its precursor, without decomposing.
13. The method according to any of the foregoing claims, wherein, before, during or after, the polymerization reaction, at least one aldehyde is added to the mixture.
14. The method according to claim 13, when dependent on claim 7, wherein the at least one aldehyde is added during step ba).
15. The method according to any of claims 13-14, wherein the at least one aldehyde is selected from the group comprising acetaldehyde, benzaldehyde, carboxybenzaldehyde, cinnamaldehyde, chlorobenzaldehyde, ferrocene carboxaldehyde, formaldehyde, furfural, glutaraldehyde, paraformaldehyde, polyhydroxyaldehyde, propionaldehyde, pyridine aldehyde, salicylaldehyde and valeraldehyde.
16. The method according to claim 15, wherein the benzaldehyde is substituted with at least one electron-donating group, selected from -NHR, -NRR', -OH, -OR, -C₆H₅, -CH₃, -

CH₂R, -CHR₂ and CR₃, wherein R and R' represent linear or branched C₁-C₁₂ alkyl groups, C₃-C₈ cycloalkyl groups, C₆-C₁₂ aralkyl groups, C₆-C₁₂ aryl groups, poly(ethylene oxide), poly(propylene oxide), and poly(ethylene oxide)-co-poly(propylene oxide)block co-polymers.

17. The method according to claim 16, wherein the at least one electron-donating group on benzaldehyde is in the para-position.
18. The method according to any of claims 16 - 17, wherein the at least one electron-donating group on benzaldehyde is -OH or -OR, wherein R represents a linear or branched C₁-C₁₂ alkyl group, a C₃-C₈ cycloalkyl group, a C₆-C₁₂ aralkyl group, a C₆-C₁₂ aryl group, poly(ethylene oxide), poly(propylene oxide), or poly(ethylene oxide)-co-poly(propylene oxide)block co-polymer.
19. The method according to any of claims 13-18, wherein the at least one aldehyde is selected from the group comprising p-anisaldehyde, 4-propoxybenzaldehyde and 4-(hexyloxy)benzaldehyde.
20. The method according to any of the foregoing claims, wherein, after step c), non-reacted monomer and/or precursor is removed from the reaction.
21. The method according to claim 20, wherein the removal occurs by a salt precipitation step, and/or by centrifugation or filtration, each of both possibilities optionally followed by washing, and/or by size separation and/or adsorption, and/or by enzymatic degradation, and/or by selective burning and/or by plasma treatment.
22. The method according to claim 21, wherein the salt precipitation occurs by addition of a salt, preferably a perchlorate salt, the filtration occurs using a membrane filter having a pore size smaller than 1 µm but larger than 0,01 µm, the size separation and/or adsorption occurs by gel-filtration, and the enzymatic degradation occurs by means of urease.
23. The method according to any of the foregoing claims, wherein after polymerization an amine-reactive compound, such as carboxylic acid anhydride, is added and reacted with the modified carbon nanotubes.

24. The method according to any of the foregoing claims, wherein the modified carbon nanotubes are dissolved in aqueous solution or in alcoholic solution, preferably methanolic solution.
25. A method of solubilizing carbon nanotubes, comprising the steps:
- Providing, in any order:
carbon nanotubes, and
urea;
 - mixing together the nanotubes and the urea;
 - heating the mixture of b).
26. The method according to claim 25, wherein the carbon nanotubes are as defined in any of claims 1 – 6.
27. The method according to any of claims 25 – 26, wherein the heating is above the melting temperature of urea.
28. The method according to claim 27, wherein the heating is in the range of approximately 130°C – 180°C, preferably approximately 150°C – 170°C, more preferably approximately 150°C – 160°C, most preferably approximately 150°C.
29. The method according to any of claims 25 – 28, wherein the heating is for approximately 1 – 60 min, preferably approximately 3 – 20 min, more preferably approximately 5 – 15 min, most preferably approximately 10 minutes.
30. The method according to any of claims 25-29, wherein at least one aldehyde is added to the mixture of b).
31. The method according to claim 30, wherein the at least one aldehyde is added to the mixture of b) before or during step c).

32. The method according to claim 31, wherein the at least one aldehyde is added during step c), preferably 1-5 minutes after step c) has been initiated, most preferably 1-3 minutes after step c) has been initiated.
33. The method according to any of claims 30-32, wherein the at least one aldehyde is selected from the group comprising acetaldehyde, benzaldehyde, carboxybenzaldehyde, cinnamaldehyde, chlorobenzaldehyde, ferrocene carboxaldehyde, formaldehyde, furfural, glutaraldehyde, paraformaldehyde, polyhydroxyaldehyde, propionaldehyde, pyridine aldehyde, salicylaldehyde and valeraldehyde.
34. The method according to claim 33, wherein the benzaldehyde is substituted with at least one electron-donating group, selected from -NHR, -NRR', -OH, -OR, -C₆H₅, -CH₃, -CH₂R, -CHR₂ and CR₃, wherein R and R' represent linear or branched C₁-C₁₂ alkyl groups, C₃-C₈ cycloalkyl groups, C₆-C₁₂ aralkyl groups, C₆-C₁₂ aryl groups, poly(ethylene oxide), poly(propylene oxide), and poly(ethylene oxide)-co-poly(propylene oxide)block co-polymers.
35. The method according to claim 34, wherein the at least one electron-donating group on benzaldehyde is in the para-position.
36. The method according to any of claims 34 - 35, wherein the at least one electron-donating group on benzaldehyde is -OH or -OR, wherein R represents a linear or branched C₁-C₁₂ alkyl group, a C₃-C₈ cycloalkyl group, a C₆-C₁₂ aralkyl group, a C₆-C₁₂ aryl group, poly(ethylene oxide), poly(propylene oxide), or poly(ethylene oxide)-co-poly(propylene oxide)block co-polymer.
37. The method according to any of claims 30-36, wherein the at least one aldehyde is selected from the group comprising p-anisaldehyde, 4-propoxybenzaldehyde and 4-(hexyloxy)benzaldehyde.
38. The method according to any of claims 25 - 37, wherein the product of step c) is dissolved in aqueous solution or alcoholic, preferably methanolic solution or a mixture of an aqueous and an alcoholic solution, and subjected to a salt precipitation step, and/or centrifugation or filtration, each of both possibilities optionally followed by washing, and/or

subjected to size separation and/or adsorption and/or enzymatic degradation, and/or selective burning, and/or plasma treatment.

39. The method according to claim 38, wherein the product of step c) is dissolved in aqueous solution or alcoholic, preferably methanolic solution or a mixture of an aqueous and an alcoholic solution, and is subjected to an evaporation step.
40. A carbon nanotube, produced by the method according to any of claims 1 – 39.
41. The carbon nanotube according to claim 40, wherein the nanotube is non-bundled.
42. The carbon nanotube according to any of claims 40 – 41, wherein it is decorated in a pearl-chain-like manner with discrete bodies, when viewed by AFM.
43. The carbon nanotube according to any of claims 40 – 41, having one or more physical characteristics selected from the group comprising:
- a solubility in water or aqueous solution of up to approximately 10 g/l and/or a solubility in methanol or methanolic solution of up to approximately 1 g/l,
 - an absorption maximum between 210 nm and 250 nm,
 - one or several or all of the following absorption maxima in the infrared in the following wavenumber regions:
3470 – 3490 cm^{-1} , 3420 – 3440 cm^{-1} , 3365 – 3385 cm^{-1} , 3330 – 3350 cm^{-1} , 3245 – 3265 cm^{-1} , 3210 – 3230 cm^{-1} , 1660 – 1680 cm^{-1} , 1610 – 1630 cm^{-1} , 1450 – 1470 cm^{-1} , 1330 – 1350 cm^{-1} and 1095 – 1115 cm^{-1} .
44. An association of carbon nanotubes according to any of claims 42 – 43, wherein the carbon nanotubes are non-bundled, but interconnected at their ends through said discrete bodies into branched structures, when viewed by AFM.
45. A carbon nanotube or an association of carbon nanotubes produced by the method according to claim 39.
46. The carbon nanotube or association of carbon nanotubes according to claim 45, which is at least partially crystalline.

47. The carbon nanotube or association of carbon nanotubes according to any of claims 45 – 46, having one or more physical characteristics selected from the group comprising:

- one or several or all of the following absorption maxima in the infrared in the following wavenumber regions:

3370 – 3390 cm^{-1} , 3205 – 3225 cm^{-1} , 3060 – 3080 cm^{-1} , 1700 – 1720 cm^{-1} ,
1680 – 1700 cm^{-1} , 1655 – 1675 cm^{-1} , 1580 – 1600 cm^{-1} , 1500 – 1520 cm^{-1} , 1440
– 1460 cm^{-1} , 1395 – 1415 cm^{-1} , 1245 – 1265 cm^{-1} , 1155 – 1175 cm^{-1} , 1020 –
1040 cm^{-1} , 845 – 865 cm^{-1} , 795 – 815 cm^{-1} ,

- having both crystalline and amorphous parts, when viewed under AFM, TEM and/or SEM.
- a solubility in water or aqueous solution of up to approximately 10 g/l and/or a solubility in methanol or methanolic solution of up to approximately 1 g/l.

48. Use of a carbon nanotube according to any of claims 40 – 43 or of an association of carbon nanotubes according to claim 44 or of a carbon nanotube or association of carbon nanotubes according to any of claims 45 – 47 in an electronic device, a nanoelectronic device, a memory element, a field emission device, a sensor, an actuator, an electromechanical device, a composite material, a coating/paint/paste, a hydrogen storage device, a battery or fuel cell, a supercapacitor, a photoelectrochemical device, a photovoltaic device, an energy conversion device, a light emitting diode, a liquid crystal display, a probe scanning probe microscopy, a non-linear optical device or antenna, or a catalyst.